

ODOR CONTROL METHOD

Field of the Invention

The present invention relates to a method for controlling objectionable
5 odors in aqueous systems. More particularly, the present invention relates to the
use of organic halogen donating species to control objectionable sulfur, nitrogen
and/or fatty acid based odors in aqueous systems.

Background of the Invention

Objectionable odors in an aqueous system such as an industrial aqueous
10 system can present both aesthetic and health concerns. For example, the presence
of sulfur species such as hydrogen sulfide, mercaptans and sulfides; nitrogen
species such as amines and indoles; and fatty acids species can give rise to
objectionable odors. The existence of such objectionable odors can be a problem
aesthetically. For example, homes, schools, parks or businesses located near an
15 industrial facility that emits hydrogen sulfide odors will find such odors
objectionable. In addition, health issues may arise. For example, the maximum
permissible 8-hour concentration for hydrogen sulfide is about 20 ppm
(Occupational Safety and Health Standards, Department of Labor, OSHA,
Federal Register, 37, 22142 (Oct. 18, 1972)). Nitrogen species such as amines
20 and indoles result in similar issues arising when present in an aqueous system.
Hydrogen sulfide is particularly problematic due to its very low odor threshold,
toxicity and because of its corrosion capability.

Odor control methods can be chemical or mechanical. Ventilation of
indoor air is often employed. If the air is vented without treatment, the
25 odoriferous air is simply diluted by the outside air so that the concentrations of
odor causing chemicals are below the detection threshold. Alternatively, exhaust
air may be treated in scrubbers, biofilters or absorption units. In scrubbers, the
water may contain chemicals which increase the efficiency and/or react with the

odor causing chemicals. For example, acid gases are often scrubbed with a caustic solution or a combination of caustic and sodium hypochlorite. In biofilters, a solid support is seeded with microbial cultures which degrade the odor causing chemicals. A variety of supports and microbes are available for both liquid and gaseous streams. Adsorption units typically contain some sort of solid sorbent such as activated carbon or other high surface area material. Other mechanical solutions to odor include electrostatic precipitation and combustion.

Many chemical treatments for odor control are masking agents. Masking agents can be applied as solids, liquids or gases. Most of the essential oils (limonene, pinene, etc.) and esters used for odor control may be considered masking agents. Masking agents do not actually react with the odor-causing chemical but decrease the perception of the odor by overpowering it. Masking agents replace the objectionable odor with a more pleasing odor. Masking agents may exacerbate problems with odors such as hydrogen sulfide by decreasing the perception of the gas without decreasing its toxicity or corrosiveness. Often, the smell of the masking agent itself can become objectionable.

Odor neutralization is a phenomenon in which odors can seem to cancel each other. Rather than overpowering an offensive odor with a more pleasing one of a masking agent, the aim of neutralization is to produce a net zero odor. In the process of neutralization, there is no chemical interaction between the odor causing chemical and the neutralizing agent. Like masking agents, they can exacerbate a problem if the odor that is neutralized is also toxic. Another disadvantage of neutralizing agents is that a multi-component odor will typically require a multi-component blend of neutralizing chemicals. To completely neutralize complex odors, individual blends of neutralizing chemicals would need to be developed for each individual application.

Many chemicals can be used to react with offensive odor. Deodorization of hydrogen sulfide can be accomplished with a pH adjustment. At high pH, the

equilibrium of the equation $H_2S \leftrightarrow H^+ + HS^-$ can be driven to form HS^- . Since HS^- is water soluble and non-volatile it does not present the same odor, toxicity and corrosive properties as H_2S . However, if pH is allowed to drop, H_2S is easily reformed. Many odors, including hydrogen sulfide can be oxidized by air or chemical oxidizing agents such as sodium hypochlorite or ozone. Oxidation by air is usually too slow and inefficient for most commercial applications. Care must be taken in handling, formulating and using oxidants such as sodium hypochlorite and ozone. Sulfide may also be precipitated with metal ions such as iron and zinc. The use of amines and aldehydes for scavenging H_2S from natural gas and crude oil is well documented, however many of the chemicals are of limited use in aqueous systems that contain a variety of odor causing chemicals.

Summary of the Invention

In general, the present invention relates to removing odors from an aqueous system by adding an effective dosage of a treatment agent to the aqueous system or spraying it into the atmosphere near the aqueous system. The problematic odors controlled by the present invention can be a result of odoriferous sulfur compounds, nitrogen compounds or fatty acid compounds present in the aqueous system. The odor control treatment of the present invention comprises a halogen donor organic molecule such as halogenated succinimides, halogenated hydantoins, halogenated isothiazolines, other halogenated organic compounds containing electron donating groups and mixtures thereof.

In accordance with the present invention, it has been found that halogen donor organic materials are effective at controlling undesirable odor of aqueous systems which results from the presence of odoriferous sulfur compounds, odoriferous nitrogen compounds and odoriferous fatty acid compounds. The

halogen donor organic materials can be added directly to the aqueous stream, added to components such as scrubbers that contact the aqueous stream or sprayed into the atmosphere near the aqueous system. The odor control of the present invention is achieved by any means of bringing the halogen donor materials into contact with the odoriferous component of the aqueous system.

In one aspect of the present invention, it has been found that halogenated succinimide materials are effective at reducing odors of aqueous systems which result from the presence of odoriferous sulfur compounds, odoriferous nitrogen compounds and odoriferous fatty acid compounds.

In a further aspect of the present invention, it has been found that objectionable hydrogen sulfide odors from an aqueous system can be controlled by the addition of at least one organic halogen donor molecule of halogenated succinimides, halogenated hydantoin, halogenated isothiazolines, other halogenated organic compounds containing electron donating groups and mixtures thereof to the aqueous system.

Detailed Description of the Invention.

The present invention involves controlling offensive odors from aqueous systems through the addition of organic halogen donor treatment agents to the aqueous system or the atmosphere near the aqueous system. Offensive odors such as odors caused by sulfur compounds, nitrogen compounds and fatty acid materials can be controlled by the method of the present invention.

Typical sulfur compounds which can cause objectionable odors when present in an aqueous system include hydrogen sulfide, mercaptans and sulfides. Typical nitrogen compounds which cause objectionable odors when present in an aqueous system include amines and indoles. Typical oxygen moieties which can cause objectionable odors when present in an aqueous system include fatty acids.

Organic halogen donor treatment agents of the present invention can include halogenated succinimides, halogenated hydantoin, halogenated

isothiazolines and other halogenated organic compounds containing electron donating groups. Typical halogenated succinimides effective in the method of the present invention include N-chlorosuccinimide and N-bromosuccinimide.

Typical halogenated hydantoins effective in the method of the present invention

5 include 1-bromo-3-chloro-5,5-dimethylhydantion and 1,3-dichloro-5,5-dimethylhydantions 1,3-dibromo-5,5-dimethylhydantion and mixtures thereof. Typical halogenated isothiazolines include 5-chloro-2-methyl-4-isothiazolin-3-one and 5-bromo-2-methyl-4-isothiazolin-3-one and mixtures thereof. Typical halogenated organic compounds containing electron donating groups effective in the method
10 of the present invention include 2,2-dibromo-3-nitropropionamide and 2-bromo-2-nitropropane-1,3-diol.

The organic halogen donating treatment agent of the present invention can be added directly to the aqueous system where odor control is desired. Addition to the aqueous system may be by direct addition or by addition to components
15 that the aqueous stream contacts. Alternatively, the treatment may be sprayed into the atmosphere near the aqueous system. The actual amount of odor control treatment necessary to achieve the desired level of odor control will vary based upon the concentration and type of odor causing species in the aqueous system. Typical dosages of organic halogen donating materials to an aqueous stream for
20 odor control within the scope of the present invention will range from about 1 to 1000 parts per million, preferably from about 1 to 500 parts per million and most preferably ranging from about 1 to 100 parts per million.

The present invention will now be further described with reference to a number of specific examples which are to be regarded as illustrative and not as
25 restricting the scope of the present invention. In the examples, hydrogen sulfide was used as the odor causing material due to its prevalence in many industrial odor situations, its low odor threshold and its obnoxious odor. In addition,

hydrogen sulfide is a toxic as well as corrosive material whose control in the industrial aqueous system is desirable.

Examples

Example 1

5 Testing was undertaken by adding sodium sulfide to a pH7 buffer solution in a closed chamber. The hydrogen sulfide concentration in the headspace was measured using an electrochemical hydrogen sulfide sensor.

10 A number of halogen donor materials were tested by adding varying dosages of treatments to the solution. Table 1 summarizes the results of the testing.

Table 1

15	<u>Treatment</u>	<u>Dosage (ppm)</u>	<u>H₂S Reading (ppm)</u>
	N-chlorosuccinimide	0	143
		2	120
		4	90
		6	70
20		8	46
		10	23
		12	5
	N-bromosuccinimide	0	143
25		4	113
		8	87
		12	59
		16	35
		20	16
30		24	8
	2-bromo-2-nitropropane-1, 3-diol	0	163
		5	104
		10	83

20	38
30	21
40	6

Table 1 continued

	<u>Treatment</u>	<u>Dosage (ppm)</u>	<u>H₂S Reading (ppm)</u>
5	2,2-dibromo-3-nitropropionamide	0	143
		1.6	132
		3.2	112
		4.8	102
10		6.4	81
		8	63
		9.6	49
		11.2	35
		12.8	23
15		14.4	16
		16	6
	5-chloro-2-methyl-4-isothiazolin-3-one		
		0	158
20		20	147
		40	104
		60	86
		80	61
		100	31
25		120	21

Example 2

Testing was undertaken using wastewater from a commercial meat processing facility. Organic halogen donor treatments were added to the wastewater in a closed chamber and hydrogen sulfide headspace concentration measurements were taken using an electrochemical hydrogen sulfide sensor. Table 2 summarizes the results.

Table 2

	<u>Treatment</u>	<u>Dosage (ppm)</u>	<u>H₂S Reading (ppm)</u>
35	N-chlorosuccinimide	0	348
		4	155
		6	39

8	28
10	18
12	5

Table 2 continued

5	<u>Treatment</u>	<u>Dosage (ppm)</u>	<u>H₂S Reading (ppm)</u>
		20	4
	2-bromo-2-nitropropane-1,3-diol	0	469
		10	216
10		12	195
		14	78
		16	62
		18	37
		20	27
15			

Example 3

Testing was undertaken using sludge from a papermill. Organic halogen donor treatment was added to the sludge in a closed chamber and hydrogen sulfide headspace concentration readings were taken using an electrochemical hydrogen sulfide sensor. Table 3 summarizes the results.

25		<u>Table 3</u>	
	<u>Treatment</u>	<u>Dosage (ppm)</u>	<u>H₂S Reading (ppm)</u>
	2-bromo-2-nitropropane-1, 3-diol	0	158
		2.5	143
		5	97
30		10	50
		15	28
		20	13
		21	

Example 4

Testing was undertaken using sludge from a municipal waste treatment facility. Organic halogen donor treatment materials were added to the sludge in a closed chamber and hydrogen sulfide headspace concentration readings were taken using an electrochemical hydrogen sulfide sensor. Table 4 summarizes the results.

Table 4

	<u>Treatment</u>	<u>Dosage (ppm)</u>	<u>H2S Reading (ppm)</u>
10	N-chlorosuccinimide	0	455
		20	453
		40	311
		50	205
		60	169
15		70	165
		100	85
		200	34
		300	12
		400	0
20	N-bromosuccinimide	0	455
		40	435
		60	415
		70	335
25		80	289
		100	218
		150	112
		200	85
		400	44
30		600	25
		800	17
		1000	12

Example 5

Testing was undertaken using wastewater from a food processing plant. Organic halogen donor treatment agents were added to the wastewater in a closed chamber and hydrogen sulfide headspace concentration readings were taken using an electrochemical hydrogen sulfide sensor. Table 5 summarizes the results.

Table 5

	<u>Treatment</u>	<u>Dosage (ppm)</u>	<u>H2S Reading (ppm)</u>
10	N-chlorosuccinimide	0	189
		12	184
		20	97
		28	46
		40	6
15	N-bromosuccinimide	90	0
		0	189
		16	113
		20	109
		28	31
20		40	35
		100	2

Example 6

Testing was undertaken using leachate from a landfill. Organic halogen donor treatments were added to the leachate in a closed chamber and hydrogen sulfide headspace concentration readings were taken using an electrochemical hydrogen sulfide sensor. Table 6 summarizes the results.

Table 6

	<u>Treatment</u>	<u>Dosage (ppm)</u>	<u>H2S Reading (ppm)</u>
30	N-chlorosuccinimide	0	181
		10	112

	50	109
	75	102
	90	21
	100	13
5	120	2
	250	0
	N-bromosuccinimide	
	0	171
	20	91
10	50	86
	100	50

Table 6 continued

	<u>Treatment</u>	<u>Dosage (ppm)</u>	<u>H2S Reading (ppm)</u>
		160	12
15		200	2
		400	0

The data in tables 1-6 show the efficiency of organic halogen donors tested in preventing airborne hydrogen sulfide and thereby inhibiting the accompanying noxious odor.

While the present invention has been described with respect to particular embodiments thereof, it is apparent that numerous other forms and modifications of this invention will be obvious to those skilled in the art. The appended claims and this invention generally should be construed to cover all such obvious forms and modifications which are within the true spirit and scope of the present invention.

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